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SYNTHESIS OF NONCRYSTALLINE AROMATIC POLYAMIDES

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Noncrystalline thermooxidatively stable aromatic polyamides were synthesized through the triphenyl phosphite-promoted polycondensations of 3,3'-[sulfonylbis(1,4-phenylenoxy)]dibenzoic acid and 3,3'-[carbonylbis(1,4-phenylenoxy)]dibenzoic acid with 3,3'-(1,3-phenylendioxy)dianiline. Alternatively, the polymers could be prepared through the low temperature polydensations in N-methylpyrollidone of the corresponding diacid chlorides with the aromatic diamine. An additional polyamide was synthesized through the self-condensation of 3-[4-(3-aminophenoxybenzoyl)phenoxy]benzoic acid. This previously unreported monomer had been prepared by a two-step reaction sequence from 4,4'-difluorobenzophenone. Inherent viscosities in the range of 0.27-0.63 dl/g (N,N-dimethylacetamide, 30° C, 0.2 g/dl) were obtained. Polymer structures were established by elemental analyses and infrared spectroscopy. Thermal characterization was carried out by differential scanning calorimetry, thermal gravimetric analysis, and isothermal aging. No evidence of crystallinity was observed and glass transition temperatures as low as 120° C were recorded. Thermooxidative degradation under

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thermal gravimetric analysis commenced in the range of 410-430° C with essentially complete weight loss being recorded at 700° C. Under isothermal aging in air at 316° C, weight losses of 20-50 percent were recorded after 200 hours.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Nonmetallic and Composite Materials", Task No. 230303, Work Unit Directive 23303Q307, "Structural Resins". It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. I. J. Goldfarb as the Materials Laboratory Project Scientist. Co-authors were Dr. R. C. Evers, Materials Laboratory (AFWAL/MLBP) and Dr. Tonson Abraham and Mr. E. J. Soloski, University of Dayton Research Institute. This report covers research conducted from January 1985 to January 1986.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

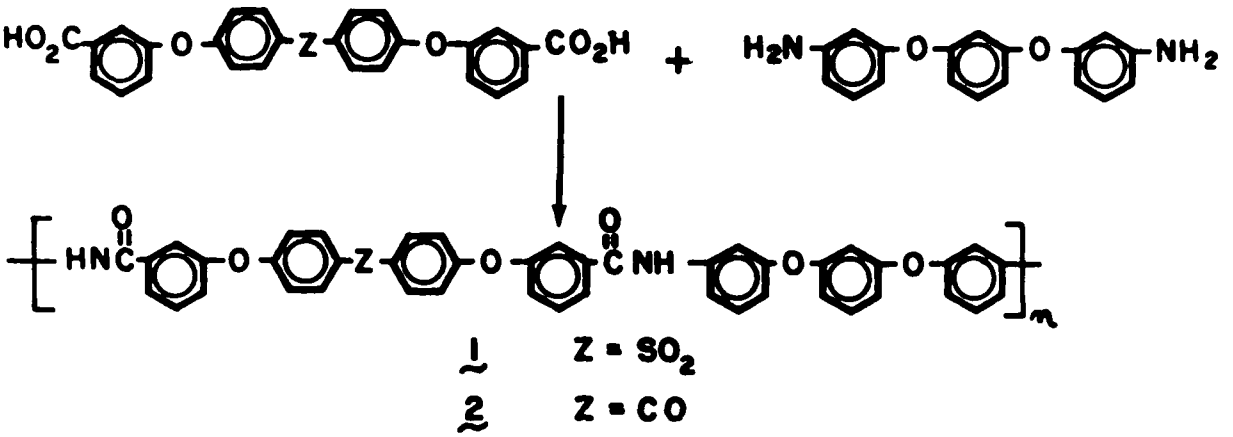
SECTION I
INTRODUCTION

Considerable effort has been expended over the last decade on research leading to the preparation of molecular composites under the Air Force Ordered Polymers Program. From this research has arisen the need for new thermoplastic polymers to act as hosts for the rod-like polymers in the molecular composites. Since the molecular composites are being processed in methanesulfonic acid, it is necessary that the thermoplastic host be soluble and chemically stable in that strongly acidic medium. Aliphatic polyamides have been used as the thermoplastic host but lack the requisite thermooxidative stability. While aromatic polyamides (polyaramides) exhibit substantially increased thermooxidative stability, they generally exhibit high glass transition temperatures (Tg's) or substantial crystallinity and are exceedingly difficult to process and consolidate when used in conjunction with a rod-like polymer in a molecular composite. The present effort is directed toward synthesis of amorphous polyaramides which exhibit low Tg's.

When compared with their crystalline counterparts, amorphous polyaramides with Tg's offer the possibility of facile processability while retaining high thermooxidative stability. In order to achieve low Tg's, polyaramides which contain both aryl sulfone and aryl ether moieties have been prepared. These efforts include the polycondensation of 4,4'-[sulfonylbis(1,4-phenylenoxy)]dibenzoyl chloride with commercially available aromatic diamines[1] and the polymerization of 4,4'-[sulfonylbis(p-phenylenoxy)dianiline with isophthaloyl- and terephthaloyl-chloride.[2] The lowest Tg attained was 230°C.

Under the current effort, amorphous polyaramides (1 and 2) with Tg's as low as 128°C have been prepared through the polycondensation of 3,3'-[sulfonylbis(1,4-phenylenoxy)]dibenzoic acid ($Z=SO_2$) and 3,3'[carbonylbis(1,4-phenylenoxy)]dibenzoic acid (Z=CO) with 3,3'-(1,3-phenylendioxy)-dianiline. The polymers were obtained by direct polycondensation of the aromatic diacids

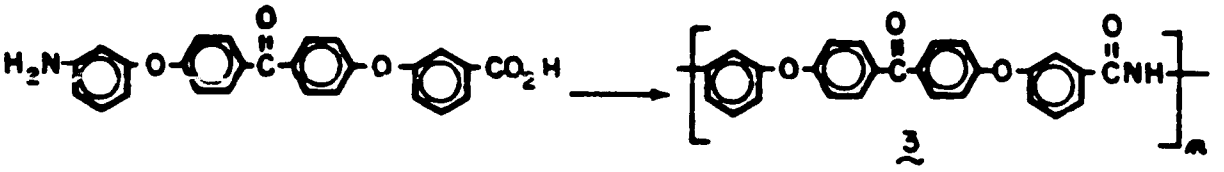
were obtained by direct polycondensation of the aromatic diacids with the aromatic diamine and, alternatively, via the low-temperature polycondensation of the corresponding diacid chlorides with the aromatic diamine.



1 Z = SO_2

2 Z = CO

In addition a previously unreported monomer, 3-[4-(3-amino-phenoxybenzoyl)-phenoxy]benzoic acid, was prepared and yielded a polyaramide (3) by the direct polycondensation route.



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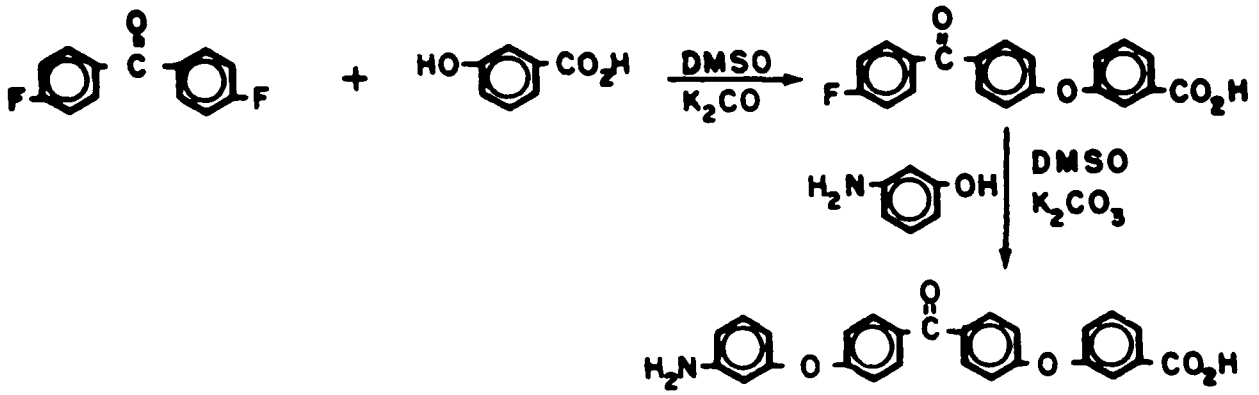
SECTION II
RESULTS AND DISCUSSION

While the requisite diacids and diacid chlorides could be prepared by a published route,[4] the synthesis of 3-[4-(3-aminophenoxybenzoyl)phenoxy]benzoic acid had not been reported and was achieved by the two-step reaction sequence shown below. No attempt was made to improve the relatively low yield (14%). Attempts to utilize this reaction sequence to prepare the analogous sulfonyl monomer through reaction of m-hydroxybenzoic acid with 4,4'-difluorodiphenylsulfone were unsuccessful due to experimental difficulties in the isolation of the intermediate monocarboxylic acid.



Polymers (1 and 2) were obtained through polycondensation of 3,3'-(1,3-phenylendioxy)dianiline with the diacid monomers in the presence of triphenyl phosphite and pyridine as well as by the low-temperature reactions of the corresponding diacid chlorides with the diamine monomers. Polymer 3 was prepared exclusively through the triphenyl phosphite-promoted polycondensation. Inherent viscosities in the range of 0.15-0.63 dl/g were recorded (Table I) with the polymers prepared from the diacid chloride monomers exhibiting significantly higher degrees of polymerization. However, no significant effort was made to maximize the polymer molecular weights.

TABLE I

PREPARATION OF AROMATIC POLYAMIDES

Polymer	Method[1]	% Yield	η_{inh}[2] dl/g	Analysis - % (Calc'd/Found) C	H	N	S
1	A	96	0.27	70.76/70.81	4.04/4.19	3.75/4.00	4.29/4.23
2	A	77	0.22	76.04/75.37	4.25/4.30	3.94/4.13	-
1	B	69	0.55				
2	B	66	0.63				
3	A	85	0.43	76.64/76.07	4.20/4.17	4.43/4.30	-

(1) Method A: Polycondensation of diacid with diamine
Method B: Polycondensation of diacid chloride with diamine

(2) N,N-dimethylacetamide, 30°C, 0.2 g/dl

Polymers 1, 2, and 3 were initially characterized by elemental analyses and infrared spectroscopy. Elemental analysis values are listed in Table I. In all cases the infrared spectra exhibited absorptions at 1660-1680 cm^{-1}, indicative of aromatic amide, as well as other absorptions consistent with the polymer structures. Thermal characterization was carried out by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and isothermal aging. Thermal characterization data are given in Table II. T_g's in the range of 128-169°C were recorded. No evidence of crystallinity was observed. After cycling within the instrument to 450°C (nitrogen atmosphere, 10°C/min), increases in Tg were observed, presumably due to initial degradation and crosslinking of the polymers. Thermogravimetric analysis (air atmosphere, 10°C/min) disclosed early weight losses of 1-5 percent, possibly due to volatiles trapped within the polymers, with polymer 2 being the least stable. Thermooxidative degradation commenced in the range of 410-430°C with essentially complete weight loss being recorded at 700°C. Under isothermal aging in air at 316°C, early weight losses possibly attributable to absorbed water were also observed. After 200 hours, weight losses of 20-50 percent were recorded with polymer 2 suffering the greatest weight loss. The TGA and

isothermal aging curves are shown in Figures 1 and 2, respectively.

TABLE II

THERMAL CHARACTERIZATION OF AROMATIC POLYAMIDES

Polymer	η_{inh} - dl/g[1]	Tg (initial)[2]	Tg (Final)[3]	T dec[4]
1	0.55	128	154	429
2	0.63	144	153	413
3	0.43	169	-	419

(1) N,N-dimethylacetamide, 30°C, 0.2 g/dl

(2) Determined in nitrogen

(3) After heating to 450°C in nitrogen

(4) As indicated by thermogravimetric analysis in air

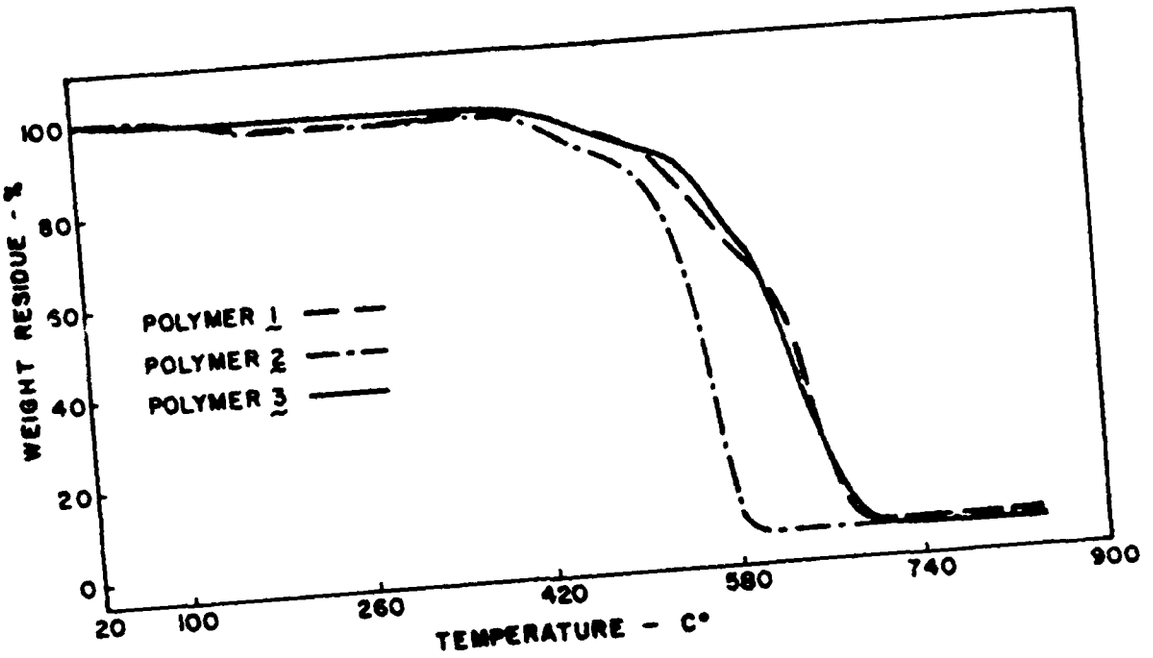


Figure 1. TGA in Air (ΔT = 10°C/min of Polymers 1-3.

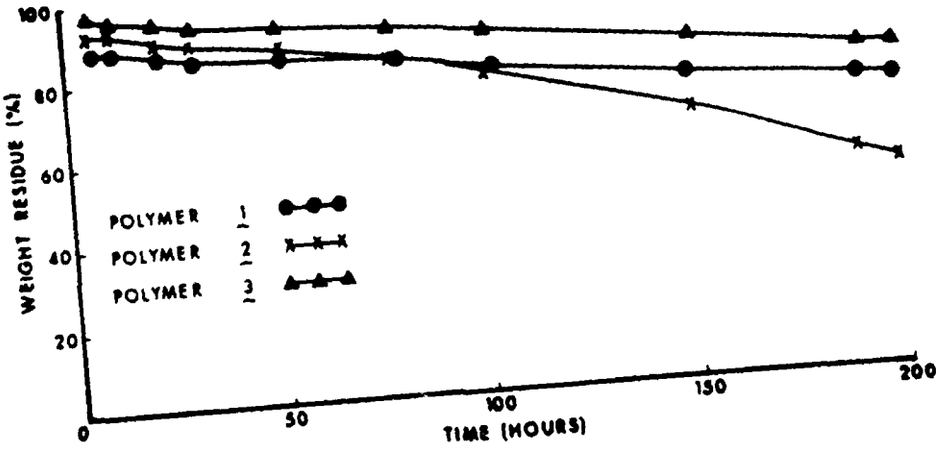


Figure 2. Isothermal Aging in Air at 316°C of Polymers 1-3.

SECTION III
CONCLUSIONS

While the thermooxidatively stable polyaramides prepared under the current effort are soluble in methanesulfonic acid, exhibit low Tg's, and show no evidence of crystallinity, they probably are not of sufficient molecular weight to lead to the degree of chain entanglement in a molecular composite necessary to give optimum mechanical properties. While the requisite advancement in molecular weight could probably be achieved through additional effort, ongoing developments in "second generation" molecular composites has largely obviated the need for the subject polyaramides.

SECTION IV
EXPERIMENTAL

1. INSTRUMENTS USED

Beckman IR 33 Spectrophotometer, Finnigan 4021 Mass Spectrometer (ionizing voltage 70 eV), duPont Differential Scanning Calorimeter 910, and duPont Thermo Gravimetric Analyzer 951.

2. MONOMERS

3,3'-(1,3-Phenylendioxy)dianiline, obtained from Millmaster Chemical Company, was dissolved in methylene chloride, filtered through a plug of silica gel, and the residue (obtained by evaporation of the filtrate) recrystallized from carbon tetrachloride to give white crystals, m.p. 106-107°C. The diacid monomers and the corresponding diacid chlorides were prepared by a published route.[4]

3-[4-(3-Aminophenoxybenzoyl)phenoxy]benzoic acid was prepared through the following procedure:

A mixture of 4,4'-difluorobenzophenone (25.2 g, 115.5 mmol), 3-hydroxybenzoic acid (8.0 g, 57.9 mmol), and anhydrous potassium carbonate (16.0 g) in dry dimethylsulfoxide (120 ml, distilled under reduced pressure from calcium hydride) was stirred by paddle at 120° under nitrogen for 48 hours. At the end of this period the reaction mixture was poured into water, and the suspension thus obtained was filtered through Celite. The clear filtrate was cooled, then carefully acidified with conc. hydrochloric acid until strongly acidic. The white precipitate that formed was filtered and recrystallized from aqueous ethanol. Two recrystallizations gave 9.5 g (48 %) of 3-[4-(4-fluorobenzoyl)-phenoxy]benzoic acid with m.p. 158.5-160°. A sample with m.p. 159-161.5° could not be purified further by recrystallization.

Anal. Calc'd for $C_{20}H_{13}FO_4$: C, 71.42; H, 3.89; F, 5.64.
Found: C, 71.39; H, 3.96; F, 5.44.

IR(KBr, strong absorptions (cm^{-1}): 3760-2140 (ν_{max} 3080), 1695, 1648, 1602, 1583, 1300, 1275, 1248, 930, 850, 760.

MS: 337 (8.6), 336 (37.5) $[M]^{\oplus}$, 242 (19.9), 241 (100) $[M-F-\phi-]^{\oplus}$, 199 (14.4) $[M-CO_2H-\phi-\underline{m}-O]^{\oplus}$, 168 (9.6) $[M]^{2\oplus}$, 123 (69.1) $[F-\phi-\underline{p}-CO]^{\oplus}$, 95 (42.7) $[F-\phi]^{\oplus}$. At higher temperature, ions resulting from the diacid are observed: 455 (5.6), 454 (18.4) $[M]^{\oplus}$, 317 (8.8) $[M-O-\phi-\underline{m}-CO_2H]^{\oplus}$, 242 (15.6), 241 (100) $[M-CO_2H-\phi-\underline{m}-O-\phi]^{\oplus}$. The intensities of peaks at 242 and 241 are increased due to some contribution from the more volatile compound 336 (13.3) $[M]^{\oplus}$.

A mixture of m-aminophenol (0.64 g, 5.87 mmol), 3-[4-(4-fluorobenzoyl)phenoxy]benzoic acid (2.0 g, 5.95 mmol), and anhydrous potassium carbonate (4.0 g) was stirred (magnetic bar) in dry dimethylsulfoxide (20 ml, distilled under reduced pressure from calcium hydride) at 120° under nitrogen for 48 hours. The cooled reaction mixture was poured into water and carefully neutralized with conc. hydrochloric acid to precipitate 2.58 g of a white solid. The crude product was digested in hot toluene, and the toluene solution (after decanting from a large quantity of gum) was allowed to stand overnight at 0°C. The crystals thus obtained were recrystallized in the same manner to give 0.35 g of product, m.p. 144-150° dec. (14%).

Anal. Calc'd for $C_{28}H_{19}NO_5$: C, 73.40; H, 4.50; N, 3.29.
Found: C, 73.53; H, 4.69; N, 3.74.

IR(KBr, strong absorbances (cm^{-1})): 3700-2200, 1705, 1650, 1600, 1585, 1505, 1490, 1447, 1310, 1280, 1245, 1160, 928, 855, 740, 675.

MS: 426 (13.9), 425 (45.9) $[M]^{\oplus}$, 242 (10.8), 241 (54.8) $[M-NH_2-\phi-\underline{m}-O-\phi-]^{\oplus}$, 236 (10.0), 213 (20.7), 212 (92.5) $[M-O-\phi-\underline{m}-CO_2H]^{\oplus}$, 184 (17.9) $[NH_2-\phi-\underline{m}-O-\phi-]^{\oplus}$, 143 (100).

3. POLYMERS

The following are representative examples of the polycondensation reactions.

Polycondensation of 3,3'-[Sulfonylbis(4-phenylenoxy)]dibenzoic Acid and 3,3'-(m-phenylendioxy)dianiline

Dried N-methylpyrrolidinone (2.0 ml, distilled under reduced pressure from calcium hydride) was added to a mixture of 3,3'-[sulfonylbis(4-phenylenoxy)]dibenzoic acid (0.6955 g, 1.48 mmol), 3,3'-(1,3-phenylendioxy)dianiline (0.4314 g, 1.48 mmol), and anhydrous lithium chloride (0.1 g). Triphenyl phosphite (0.37 ml) and dry pyridine (0.5 ml, distilled from calcium hydride) were also added. The reaction mixture was heated under nitrogen with stirring (magnetic bar) to 100° for 4 hours. As the polycondensation proceeded, the solution became viscous and the lithium chloride suspension dissolved. The polyamide was isolated as a stringy mass by precipitation from methanol. It was purified by reprecipitation from methanol after redissolution in dimethylacetamide (4.0 ml). The product (1.01 g, 96% yield) was dried overnight at 100°C (0.1 mm Hg) and exhibited an inherent viscosity of 0.27 dl/g (N,N-dimethylacetamide, 30°C, 0.2 g/dl).

Anal. Calc'd for $(C_{44}H_{30}N_2SO_8)_n$: C, 70.76; H, 4.04; N, 3.75; S, 4.29.

Found: C, 70.81; H, 4.19; N, 4.00; S, 4.23.

Polycondensation of 3,3'-[Sulfonylbis(4-phenylenoxy)]dibenzoyl chloride and 3,3-(m-phenylendioxy)dianiline

A mixture of 3,3'-[sulfonylbis(4-phenylenoxy)]dibenzoyl chloride (0.4134 g, 0.785 mmol) and 3,3'-(1,3-phenylendioxy)-dianiline (0.2291 g, 0.785 mmol) was cooled to -78° under nitrogen. Dry N-methylpyrrolidinone (4.5 ml, distilled under reduced pressure from calcium hydride) and propylene oxide (0.33 ml) were then added. After a few minutes, the cooling bath was removed and the contents of the flask stirred (magnetic bar) while being allowed to warm to room temperature. After being stirred overnight, the viscous solution was poured into methanol, with stirring, to yield a stringy mass. The polymer was purified by reprecipitation from methanol after redissolution in dimethylacetamide (4.0 ml). The product (0.4 g, 69%) was dried overnight at 100° (0.1 mm Hg). An inherent viscosity of 0.55 dl/g (N,N-dimethylacetamide, 30°C, 0.2 g/dl) was recorded.

Anal. Calc'd for $(C_{44}H_{30}N_2SO_8)_n$: C, 70.76; H, 4.04; N, 3.75; S, 4.29.

Found: C, 70.58; H, 4.00; N, 3.90; S, 4.18.

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